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(54) **Releasably bound carboxylic acids.**

(57) This invention relates to a composition for and method of storing and using acetic acid or propionic acid, the composition comprising an alkali(ne earth) metal salt of acetic acid or propionic acid and an aliphatic carboxylic acid which has a pKa value lower than that of acetic acid or propionic acid respectively. When this composition is brought into contact with a solvent system capable of allowing ionisation of the salt and the aliphatic carboxylic acid, free acetic acid or propionic acid is released *in situ*. This method enables the free acids to be stored and released at the point of use thereby substantially reducing the risks of corrosion and unpleasant odours.

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This invention relates to a method of storing and using acetic or propionic acid releasably bound on a support.

It is well known that acetic acid propionic acids are relatively strong organic acids which are also corrosive. Yet these acids have a considerable number of uses, not least in the field of agriculture e.g. for the protection of crops, preparation of silage and as a salmonella control agent. However, the storage and transportation of acetic acid and propionic acids is rather difficult due to their corrosivity and their pungent smell. Various methods have been tried to immobilize acetic and propionic acids but with inadequate success either because of the strong bond formed between these acids and the support thereby not being readily releasable at the point of use or because of a relatively weak bond whereby the acid evaporates from the support too readily and hence results in loss of the acid and risks polluting the environment surrounding the point of storage.

It has now been found that these problems can be mitigated by using an alkali(ne earth) metal propionate with another carboxylic acid of defined physical properties such that free acetic acid or propionic acid is released at the point of use.

Accordingly the present invention is a composition comprising an acetate or a propionate salt of an alkali(ne earth) metal and an aliphatic carboxylic acid which has a lower pKa value than that of acetic acid or propionic acid respectively.

A feature of the invention is that the alkali(ne earth) acetates or propionates when used in a medium capable of allowing dissociation of the salt of free carboxylic acids into anions and cations e.g. in aqueous systems, also dissociates into the alkali(ne earth) metal ions and acetate or propionate ions and the aliphatic carboxylic acid in turn dissociates into the corresponding carboxylate ion and hydrogen ions. However, due to the relative differences in the pKa values, the aliphatic carboxylate ion combines with the alkali(ne earth) metal ion to form the alkali(ne earth) metal salt of the aliphatic carboxylic acid and releases acetic or propionic acid in situ.

The process works particularly efficiently if the alkali(ne earth) metal salt of the aliphatic carboxylic acid so formed is readily soluble in the solvent system used to generate the desired acetic or propionic acid. However, for practical reasons it may be preferable, though not essential, to form a substantially insoluble alkali(ne earth) metal salt in order to enable easy separation of the acetic or propionic acid solution from the insoluble salt by decantation or filtration immediately prior to use. Such an insoluble salt can be formed by the appropriate selection of reagents and/or solvents. It should be noted, however, that in the process of separating the acetic or propionic acid solution from the precipitate, some of the yield of available acetic or propionic acid may be lost due to occlusion on the precipitate.

Particularly suitable alkali(ne earth) metal salts for use in the compositions of the present invention are those of sodium, potassium, calcium and magnesium.

Propionic acid has a pKa value (i.e. dissociation constant) of about 4.87 in water at 25°C. Thus any aliphatic carboxylic acid which has a lower pKa value under comparable conditions would be suitable for admixing with the alkaline earth metal propionate.

Similarly, acetic acid has a pKa value (i.e. dissociation constant) of about 4.75 in water at 25°C. Thus any aliphatic carboxylic acid which has a lower pKa value under comparable conditions would be suitable for admixing with the alkaline earth metal acetate.

Such aliphatic carboxylic acids which have a pKa value lower than that of acetic or propionic acid may be mono-, di- or poly-carboxylic acids and may be saturated or unsaturated. Particularly suitable for this purpose are the di- and polycarboxylic acids, especially the unsaturated carboxylic acids due to their ability to form alkaline earth metal salts which have very low solubility in aqueous systems, e.g. water. Specific examples of the preferred aliphatic carboxylic acids include transfumaric acid (pKa 3.03 and 4.44), furoic acid (pKa 3.17), furan carboxylic acid (pKa 3.15) lactic acid (pKa 3.08), maleic acid (pKa 1.83), malic acid (pKa 3.40), oxalic acid (pKa 1.23), malonic acid (pKa 2.38), succinic acid (pKa 4.16), suberic acid (pKa 4.52), mesaconic acid (pKa 3.09 and 4.75), methyl malonic acid (pKa 3.07), methyl succinic acid (pKa 4.13), gallic acid (pKa 4.41), alpha-tartaric acid (pKa 2.98) and meso-tartaric acid (pKa 3.22).

For instance, if fumaric acid, which has a substantially low volatility, is intimately mixed with a calcium acetate or calcium propionate salt and stored as such the problems of odour and corrosivity are immediately alleviated. However, when the fumaric acid admixed with calcium acetate or calcium propionate is brought into contact with a suitable solvent, e.g. water, at the point of use and at room temperature, then a rapid exchange of ions takes place and the respective acetic or propionic acid is liberated immediately into the aqueous solution in situ leaving behind a substantially insoluble precipitate of calcium fumarate which can be readily removed either by decantation or filtration.

The filtrate containing the acetic or propionic acid in solution and some calcium fumarate can then be used as desired.

The above reaction can be represented as follows:



The alkali(ne earth) metal acetate or propionate and the aliphatic carboxylic acid in the composition may be combined together in various ways. For instance, if the aliphatic carboxylic acid is a solid, this can be intimately mixed with the calcium propionate and form a solid mixture. However, if the aliphatic carboxylic is a liquid, this liquid can be used to impregnate the solid calcium acetate or propionate. The admixed or impregnated calcium acetate or propionate can then be stored and used as desired.

The amount of aliphatic carboxylic acid present in the composition along with the respective alkali(ne earth) metal acetate or propionate salt is limited only by the physical ability of the two to be admixed or for the former to be impregnated on the latter. The acetate or propionate salt may, for instance be admixed or impregnated with 1 to 90% w/w, preferably 40-60% w/w of the aliphatic carboxylic acid based on the total weight of the alkali(ne earth) metal acetate or propionate. An equimolar mixture of the aliphatic carboxylic acid and the acetate or propionate salt is most preferred.

Each of the alkali(ne earth) metal acetate or propionate and the aliphatic carboxylic acid admixed therewith may be, if not a liquid, in the form of a powder or granules or can be shaped into any other convenient shape or form e.g. pellets. The physical shape of the two will be determined by the desired speed of release of the desired acetic or propionic acid once in contact with the appropriate solvent system. It would be clear that for a slow release system, the admixture of the two will be highly compacted.

Whichever form of the components is used in the composition, it will be clear that in order for the acetic acid or propionic acid to be released from the salt, the admixture has to be brought into contact with an aqueous or non-aqueous system, e.g. water, which is capable of allowing the salt and the carboxylic acid to dissociate in said system. Upon intimately mixing the alkali(ne earth) metal acetate or propionate and the aliphatic carboxylic acid with the solvent system, the exchange of ions takes place.

Thus according to a further embodiment, the present invention is a method of releasing free acetic acid or propionic acid *in situ* in a solvent system capable of allowing the respective acetate or propionate salt of an alkali(ne earth) metal and an aliphatic carboxylic acid having a lower pKa value than that of acetic acid or propionic acid respectively to ionise in said system, said method comprising bringing into contact with the solvent system a composition comprising said acetate or propionate salt and said aliphatic carboxylic acid, thereby generating a solution comprising free acetic or propionic acid respectively in said solvent system.

The following Examples will, for the sake of convenience, be directed to the impregnation of calcium acetate or propionate with fumaric acid but should in no way be construed as limiting the inventive concept disclosed herein.

#### Example 1

1.5g of 63:67 (w:w) mixture of calcium propionate and fumaric acid were mixed. The mixture was suspended in 100ml demineralised water in a beaker. After 1 or 2 hours of stirring the sample was transferred to a 250ml volumetric flask and water was added to 250ml. After homogenisation, the solution was filtered over a 0.2 microns filter. The propionic acid content in the filtrate was determined by gas chromatography, in five-fold. Quantitative measurements were carried out by external standardisation, i.e. by comparison of the peak area of the sample with that of a propionic acid standard solution of 4mg/ml. The quantity of propionic acid formed was calculated as follows: mg propionic acid found =

$$\text{mg propionic acid found} = \frac{\text{peak area sample}}{\text{peak area standard}} \times C_{\text{st}} \times V_{\text{m}}$$

where

$C_{\text{st}}$  = concentration of the standard (4 mg/ml)

$V_{\text{m}}$  = volume of the flask (250 ml)

The experiment was carried out on 3 different samples of calcium propionate, A, B and C, each in two-fold.

The maximal concentration of propionic acid that can be obtained is calculated as follows:

$$\text{mg propionic acid max} = \text{intake (mg)} \times P_{\text{cp}} + \times C_{\text{v}} \times P_{\text{prop}} \times C_{\text{c}}$$

in which intake = mg sample

$P_{\text{cp}}$  = % calcium propionate in the sample/100 (=0.63)

$C_{\text{v}}$  = correction factor for water content of the sample (= 0.95)

$P_{\text{prop}}$  = % propionate in calcium propionate/100 (= 0.784)

$C_{\text{c}}$  = correction factor for the conversion of propionate to propionic acid (= 1.013)

The yield of the reaction =  $\frac{\text{mg propionic acid found}}{\text{mg propionic acid max.}}$

The results are given in Table 1.

TABLE I

Sample	Intake	Peak area (10 <sup>3</sup> )	propionic acid found	propionic acid max.	yield (%)
standard 4 mg/ml		546.5			
A	1	1561.3	402.5	736	99.2
1hr stirring	2	1711.1	437.5	801	98.5
standard 4 mg/ml		561.5			
A	1	1565.2	403.3	718	96.5
2hr stirring	2	1680.1	449.2	800	100.1
standard 4 mg/ml		535.7			
B	1	1519.3	313.6	585	81.1
	2	1772.2	344.7	644	76.4
standard 4 mg/ml		535.7			
C	1	1444.2	368.9	689	100.3
	2	1458.7	383.9	717	103.4

### Example 2

1.5g of 58:42 (w:w) mixture of calcium acetate and fumaric acid were mixed. The mixture was suspended in 100ml demineralised water in a beaker. After 1 hour of stirring the sample was transferred to a 250ml volumetric flask and water was added to 250ml. After homogenisation, the solution was filtered over a 0.2 microns filter. The acetic acid content in the filtrate was determined by gas chromatography, in five-fold. Quantitative measurements were carried out by external standardisation, i.e. by comparison of the peak area of the sample with that of an acetic acid standard solution of 4mg/ml. The quantity of acetic acid formed was calculated as follows:

$$\text{mg acetic acid found} = \frac{\text{peak area sample}}{\text{peak area standard}} \times C_{st} \times V_m$$

where

$C_{st}$  = concentration of the standard (4 mg/ml)

$V_m$  = volume of the flask (250ml)

The experiment was carried out on 3 different samples of calcium propionate, A, B and C, each in two fold.

The maximal concentration of acetic acid that can be obtained is calculated as follows:

$$\text{mg acetic acid max} = \text{intake (mg)} \times P_{ca} \times C_v \times P_{acet} \times C_c$$

in which intake = mg sample

$P_{ca}$  = % calcium acetate in the sample/100 (= 0.573)

$C_v$  = correction factor for water content of the sample (=0.945)

$P_{acet}$  = % acetate in calcium acetate/100 (= 0.746)

$C_c$  = correction factor for the conversion of acetate to acetic acid (= 1.010)

$$\text{The yield of the reaction} = \frac{\text{mg acetic acid found}}{\text{mg acetic acid max.}}$$

The results are given in Table 2 below.

Table 2

Sample		Intake	peak area (10 <sup>3</sup> )	acetic acid found	acetic acid max.	yield (%)
A	standard 4 mg/ml		321.4			
	1	1640.3	229.5	671	714	94.0
	2	1507.6	198.9	618	619	99.8

## Claims

1. A composition comprising an acetate or a propionate salt of an alkali(ne earth) metal and an aliphatic carboxylic acid which has a lower pKa value than that of the acetic acid or propionic acid respectively.
2. A composition according to Claim 1 wherein said composition comprises
  - a. an alkali(ne earth) metal salt of acetic acid or propionic acid,
  - b. an aliphatic carboxylic acid having a pKa value lower than that of acetic acid or propionic acid respectively and
  - c. a solvent system capable of allowing ionisation of the alkali(ne earth) metal salt and the aliphatic carboxylic acid
 such that when components (a), (b) and (c) are brought together, free acetic acid or propionic acid respectively is released into the solvent system.
3. A composition according to Claim 1 or 2 wherein the alkali(ne earth) metal salt is that of sodium, potassium, calcium or magnesium.
4. A composition according to any one of the preceding Claims wherein the aliphatic carboxylic acid having a pKa lower than acetic acid or propionic acid respectively is a saturated or unsaturated, mono-, di- or poly-carboxylic acid.
5. A composition according to any one of the preceding Claims wherein the aliphatic carboxylic acid having a pKa value lower than that of acetic or propionic acid is selected from the group consisting of transumaric acid, furoic acid, furan carboxylic acid, lactic acid, maleic acid, malic acid, oxalic acid, malonic acid, succinic acid, methylmalonic acid, methyl succinic acid, gallic acid,  $\alpha$ -tartaric acid and meso-tartaric acid.
6. A composition according to any one of the preceding Claims wherein the amount of aliphatic carboxylic acid having a lower pKa value than that of acetic acid or propionic acid respectively present in the composition with respect to the alkali(ne earth) metal salt of acetic or propionic acid is in the range from 1 to 90% by weight.
7. A composition according to any one of the preceding Claims wherein each of the alkali(ne earth) metal salt of acetic or propionic acid and the aliphatic carboxylic acid having a lower pKa value than acetic or propionic acid respectively is in a form which is the same or different and is selected from liquid, solution, powder, granules or shaped pellets.
8. A method of releasing free acetic acid or propionic acid *in situ* in a solvent system capable of allowing the respective acetate or propionate salt of an alkali(ne earth) metal and an aliphatic carboxylic acid having a lower pKa value than that of acetic acid or propionic acid respectively to ionise in said system, said method comprising bringing into contact with the solvent system a composition comprising said acetate or propionate salt and said aliphatic carboxylic acid according to any one of the preceding Claims 1-7, thereby generating a solution comprising free acetic acid or propionic acid respectively in said solvent system.



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# EUROPEAN SEARCH REPORT

Application Number  
EP 93 30 7486

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
Y	US-A-4 401 624 (ATWATER) * claims 1-5 *	1-4,6-8	C07C53/10 C07C53/122 C07C53/08 C07C51/64
Y	GB-A-1 505 388 (BP CHEMICALS LTD.) * claims 1-10 *	1-4,6-8	
Y	PATENT ABSTRACTS OF JAPAN vol. 7, no. 213 (C-187)(1358) 20 September 1983 & JP-A-58 113 143 (UENO SEIYAKU OUYOU KENKYUSHO K.K.) 5 July 1983 * abstract *	1-4,6-8	
A	SOVIET PATENTS ABSTRACTS Week 9236, 21 October 1992 Derwent Publications Ltd., London, GB; AN 92-298506 & SU-A-1 694 568 (RYABUKHA) 30 November 1991 * abstract *	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			C07C C07B
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		15 December 1993	Klag, M
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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